



Techniques of Water-Resources Investigations of the United States Geological Survey

Chapter B7

ANALYTICAL SOLUTIONS FOR ONE-, TWO-, AND THREE-DIMENSIONAL SOLUTE TRANSPORT IN GROUND-WATER SYSTEMS WITH UNIFORM FLOW

By Eliezer J. Wexler

Book 3

APPLICATIONS OF HYDRAULICS

U.S. DEPARTMENT OF THE INTERIOR
MANUEL LUJAN, Jr., *Secretary*

U.S. GEOLOGICAL SURVEY
Dallas L. Peck, *Director*

UNITED STATES GOVERNMENT PRINTING OFFICE: 1992

For sale by Book and Open-File Report Sales, U.S. Geological Survey,
Federal Center, Box 25425, Denver, CO 80225

PREFACE

The series of manuals on techniques describes procedures for planning and executing specialized work in water-resources investigations. The material is grouped under major subject headings called books and further subdivided into sections and chapters; section B of book 3 is on ground-water techniques.

The unit of publication, the chapter, is limited to a narrow field of subject matter. This format permits flexibility in revision and publication as the need arises. Chapter 3B7 deals with analytical solutions to the solute-transport equation for a variety of boundary condition types and solute-source configurations in one-, two-, and three-dimensional systems with uniform ground-water flow.

Provisional drafts of chapters are distributed to field offices of the U.S. Geological Survey for their use. These drafts are subject to revision because of experience in use or because of advancement of knowledge, techniques, or equipment. After the technique described in a chapter is sufficiently developed, the chapter is published and is for sale from the U.S. Geological Survey, Book and Open-File Report Sales, Federal Center, Box 25425, Denver, CO 80225.

Copies of the computer codes and sample data sets described in this report are available on diskette from Book and Open-File Report Sales as USGS Open File Report 92-78. They are on a 5.25" (360K) double-density diskette formatted for the IBM PC. The computer programs were originally written for a Prime minicomputer but all programs should run using IBM-PC Fortrans with minor modifications as described in the report. The plot routines were written with DISSPLA software calls and can be used on the PC only with the PC version of the DISSPLA library. Alternatively, data can be easily extracted from the program output and plotted using PC graphics presentation programs.

Reference to trade names, commercial products, manufacturers, or distributors in this manual constitutes neither endorsement by the U.S. Geological Survey nor recommendation for use.

TECHNIQUES OF WATER-RESOURCES INVESTIGATIONS OF THE U.S. GEOLOGICAL SURVEY

The U.S. Geological Survey publishes a series of manuals describing procedures for planning and conducting specialized work in water-resources investigations. The manuals published to date are listed below and may be ordered by mail from the **U.S. Geological Survey, Books and Open-File Reports Section, Federal Center, Box 25425, Denver, Colorado 80225** (an authorized agent of the Superintendent of Documents, Government Printing Office).

Prepayment is required. Remittance should be sent by check or money order payable to U.S. Geological Survey. Prices are not included in the listing below as they are subject to change. **Current prices can be obtained** by writing to the USGS address shown above. Prices include cost of domestic surface transportation. For transmittal outside the U.S.A. (except to Canada and Mexico) a surcharge of 25 percent of the net bill should be included to cover surface transportation. When ordering any of these publications, please give the title, book number, chapter number, and "U.S. Geological Survey Techniques of Water-Resources Investigations."

- TWRI 1-D1. Water temperature—influential factors, field measurement, and data presentation, by H.H. Stevens, Jr., J.F. Ficke, and G.F. Smoot. 1975. 65 pages.
- TWRI 1-D2. Guidelines for collection and field analysis of ground-water samples for selected unstable constituents, by W.W. Wood. 1976. 24 pages.
- TWRI 2-D1. Application of surface geophysics to ground-water investigations, by A.A.R. Zohdy, G.P. Eaton, and D.R. Mabey. 1974. 116 pages.
- TWRI 2-D2. Application of seismic-refraction techniques to hydrologic studies, by F.P. Haeni. 1988. 86 pages.
- TWRI 2-E1. Application of borehole geophysics to water-resources investigations, by W.S. Keys and L.M. MacCary. 1971. 126 pages.
- TWRI 2-E2. Borehole geophysics applied to ground-water investigations, by W. Scott Keys. 1990. 150 pages.
- TWRI 2-F1. Application of drilling, coring, and sampling techniques to test holes and wells, by Eugene Shuter and Warren E. Teasdale. 1989. 97 pages.
- TWRI 3-A1. General field and office procedures for indirect discharge measurements, by M.A. Benson and Tate Dalrymple. 1967. 30 pages.
- TWRI 3-A2. Measurement of peak discharge by the slope-area method, by Tate Dalrymple and M.A. Benson. 1967. 12 pages.
- TWRI 3-A3. Measurement of peak discharge at culverts by indirect methods, by G.L. Bodhaine. 1968. 60 pages.
- TWRI 3-A4. Measurement of peak discharge at width contractions by indirect methods, by H.F. Matthai. 1967. 44 pages.
- TWRI 3-A5. Measurement of peak discharge at dams by indirect methods, by Harry Hulsing. 1967. 29 pages.
- TWRI 3-A6. General procedure for gaging streams, by R.W. Carter and Jacob Davidian. 1968. 13 pages.
- TWRI 3-A7. Stage measurements at gaging stations, by T.J. Buchanan and W.P. Somers. 1968. 28 pages.
- TWRI 3-A8. Discharge measurements at gaging stations, by T.J. Buchanan and W.P. Somers. 1969. 65 pages.
- TWRI 3-A9.¹ Measurement of time of travel in streams by dye tracing, by F.A. Kilpatrick and J.F. Wilson, Jr. 1989. 27 pages.
- TWRI 3-A10. Discharge ratings at gaging stations, by E.J. Kennedy. 1984. 59 pages.
- TWRI 3-A11. Measurement of discharge by moving-boat method, by G.F. Smoot and C.E. Novak. 1969. 22 pages.
- TWRI 3-A12. Fluorometric procedures for dye tracing, Revised, by J.F. Wilson, Jr., E.D. Cobb, and F.A. Kilpatrick. 1986. 41 pages.
- TWRI 3-A13. Computation of continuous records of streamflow, by E.J. Kennedy. 1983. 53 pages.
- TWRI 3-A14. Use of flumes in measuring discharge, by F.A. Kilpatrick, and V.R. Schneider. 1983. 46 pages.
- TWRI 3-A15. Computation of water-surface profiles in open channels, by Jacob Davidian. 1984. 48 pages.
- TWRI 3-A16. Measurement of discharge using tracers, by F.A. Kilpatrick and E.D. Cobb. 1985. 52 pages.
- TWRI 3-A17. Acoustic velocity meter systems, by Antonius Laenen. 1985. 38 pages.
- TWRI 3-A18. Determination of stream reaeration coefficients by use of tracers, by F.A. Kilpatrick, R.E. Rathbun, N. Yotsukura, G.W. Parker, and L.L. DeLong. 1989. 52 pages.
- TWRI 3-A19. Levels at streamflow gaging stations, by E.J. Kennedy. 1990. 31 pages.
- TWRI 3-B1. Aquifer-test design, observation, and data analysis, by R.W. Stallman. 1971. 26 pages.
- TWRI 3-B2.² Introduction to ground-water hydraulics, a programmed text for self-instruction, by G.D. Bennett. 1976. 172 pages.

¹This manual is a revision of "Measurement of Time of Travel and Dispersion in Streams by Dye Tracing," by E.F. Hubbard, F.A. Kilpatrick, L.A. Martens, and J.F. Wilson, Jr., Book 3, Chapter A9, published in 1982.

²Spanish translation also available.

- TWRI 3-B3. Type curves for selected problems of flow to wells in confined aquifers, by J.E. Reed. 1980. 106 pages.
- TWRI 3-B4. Regression modeling of ground-water flow, by Richard L. Cooley and Richard L. Naff. 1990. 232 pages.
- TWRI 3-B5. Definition of boundary and initial conditions in the analysis of saturated ground-water flow systems—An introduction, by O. Lehn Franke, Thomas E. Reilly, and Gordon D. Bennett. 1987. 15 pages.
- TWRI 3-B6. The principle of superposition and its application in ground-water hydraulics, by Thomas E. Reilly, O. Lehn Franke, and Gordon D. Bennett. 1987. 28 pages.
- TWRI 3-B7. Analytical solutions for one-, two-, and three-dimensional solute transport in ground-water systems with uniform flow, by Eliezer J. Wexler. 1991. 193 pages.
- TWRI 3-C1. Fluvial sediment concepts, by H.P. Guy. 1970. 55 pages.
- TWRI 3-C2. Field methods of measurement of fluvial sediment, by H.P. Guy and V.W. Norman. 1970. 59 pages.
- TWRI 3-C3. Computation of fluvial-sediment discharge, by George Porterfield. 1972. 66 pages.
- TWRI 4-A1. Some statistical tools in hydrology, by H.C. Riggs. 1968. 39 pages.
- TWRI 4-A2. Frequency curves, by H.C. Riggs, 1968. 15 pages.
- TWRI 4-B1. Low-flow investigations, by H.C. Riggs. 1972. 18 pages.
- TWRI 4-B2. Storage analyses for water supply, by H.C. Riggs and C.H. Hardison. 1973. 20 pages.
- TWRI 4-B3. Regional analyses of streamflow characteristics, by H.C. Riggs. 1973. 15 pages.
- TWRI 4-D1. Computation of rate and volume of stream depletion by wells, by C.T. Jenkins. 1970. 17 pages.
- TWRI 5-A1. Methods for determination of inorganic substances in water and fluvial sediments, by Marvin J. Fishman and Linda C. Friedman, editors. 1989. 545 pages.
- TWRI 5-A2. Determination of minor elements in water by emission spectroscopy, by P.R. Barnett and E.C. Mallory, Jr. 1971. 31 pages.
- TWRI 5-A3.¹ Methods for the determination of organic substances in water and fluvial sediments, edited by R.L. Wershaw, M.J. Fishman, R.R. Grabbe, and L.E. Lowe. 1987. 80 pages.
- TWRI 5-A4.² Methods for collection and analysis of aquatic biological and microbiological samples, by L.J. Britton and P.E. Greeson, editors. 1989. 363 pages.
- TWRI 5-A5. Methods for determination of radioactive substances in water and fluvial sediments, by L.L. Thatcher, V.J. Janzer, and K.W. Edwards. 1977. 95 pages.
- TWRI 5-A6. Quality assurance practices for the chemical and biological analyses of water and fluvial sediments, by L.C. Friedman and D.E. Erdmann. 1982. 181 pages.
- TWRI 5-C1. Laboratory theory and methods for sediment analysis, by H.P. Guy. 1969. 58 pages.
- TWRI 6-A1. A modular three-dimensional finite-difference ground-water flow model, by Michael G. McDonald and Arlen W. Harbaugh. 1988. 586 pages.
- TWRI 6-A2. Documentation of a computer program to simulate aquifer-system compaction using the modular finite-difference ground-water flow model, by S.A. Leake and D.E. Prudic. 1991. 68 pages.
- TWRI 7-C1. Finite difference model for aquifer simulation in two dimensions with results of numerical experiments, by P.C. Trescott, G.F. Pinder, and S.P. Larson. 1976. 116 pages.
- TWRI 7-C2. Computer model of two-dimensional solute transport and dispersion in ground water, by L.F. Konikow and J.D. Bredehoeft. 1978. 90 pages.
- TWRI 7-C3. A model for simulation of flow in singular and interconnected channels, by R.W. Schaffranek, R.A. Baltzer, and D.E. Goldberg. 1981. 110 pages.
- TWRI 8-A1. Methods of measuring water levels in deep wells, by M.S. Garber and F.C. Koopman. 1968. 23 pages.
- TWRI 8-A2. Installation and service manual for U.S. Geological Survey monometers, by J.D. Craig. 1983. 57 pages.
- TWRI 8-B2. Calibration and maintenance of vertical-axis type current meters, by G.F. Smoot and C.E. Novak. 1968. 15 pages.

¹This manual is a revision of TWRI 5-A3, "Methods of Analysis of Organic Substances in Water," by Donald F. Goerlitz and Eugene Brown, published in 1972.

²This manual supersedes TWRI 5-A4, "Methods for collection and analysis of aquatic biological and microbiological samples," edited by P.E. Greeson and others, published in 1977.

CONTENTS

	Page		Page
Abstract.....	1	One-dimensional solute transport—Continued	
Introduction.....	1	Semi-infinite system with third-type source boundary	
Purpose and scope	2	condition—Continued	
Previous studies	2	Sample problem 4	24
Acknowledgments.....	2	Two-dimensional solute transport	24
Theoretical background.....	2	Aquifer of infinite areal extent with continuous point	
Advection.....	2	source	26
Molecular diffusion.....	3	Governing equation	26
Mechanical dispersion.....	3	Analytical solution	27
Hydrodynamic dispersion.....	4	Description of program POINT2	27
Advective-dispersive solute-transport equation.....	4	Main program	27
Chemical transformation	5	Subroutine CNRML2	31
Linear equilibrium adsorption.....	5	Sample problem 5	31
Ion exchange	6	Aquifer of finite width with finite-width solute source.....	31
First-order chemical reactions.....	6	Governing equation.....	31
Initial conditions.....	7	Analytical solution	33
Boundary Conditions.....	7	Description of program STRIPP	33
Inflow boundary	7	Main program	33
Outflow boundary	8	Subroutine CNRMLF.....	33
Lateral boundaries.....	8	Sample problem 6	33
Superposition	8	Aquifer of infinite width with finite-width solute	
One-dimensional solute transport.....	11	source.....	36
Finite system with first-type source boundary		Governing equation.....	36
condition	12	Analytical solution	36
Governing equation.....	12	Description of program STRIPI	36
Analytical solution	12	Main program	36
Description of program FINITE	13	Subroutine CNRML1	37
Main program	13	Sample problem 7	38
Subroutines ROOT1 and CNRML1.....	13	Aquifer of infinite width with solute source having	
Sample problems 1a and 1b	13	gaussian concentration distribution	38
Finite system with third-type source boundary		Governing equation.....	38
condition	17	Analytical solution	38
Governing equation.....	17	Description of program GAUSS	40
Analytical solution	17	Main program	40
Description of program FINITE	18	Subroutine CNRMLG.....	40
Subroutines ROOT3 and CNRML3.....	18	Sample problems 8a and 8b	40
Sample problem 2	18	Three-dimensional solute transport	42
Semi-infinite system with first-type source boundary		Aquifer of infinite extent with continuous point source....	42
condition	18	Governing equation.....	42
Governing equation.....	18	Analytical solution	43
Analytical solution	18	Description of program POINT3	47
Description of program SEMINF	20	Main program	47
Main program	20	Subroutine CNRML3	47
Subroutine CNRML1	20	Sample problem 9	47
Sample problems 3a and 3b	20	Aquifer of finite width and height with finite-width and	
Semi-infinite system with third-type source boundary		finite-height solute source	49
condition	21	Governing equation.....	49
Governing equation.....	21	Analytical solution	51
Analytical solution	21	Description of program PATCHF.....	51
Description of program SEMINF	24	Main program	51
Subroutine CNRML3	24	Subroutine CNRMLF.....	51

	Page		Page
Three-dimensional solute transport—Continued		Description of subroutines—Continued	
Aquifer of finite width and height with finite-width and finite-height solute source—Continued		Input/Output subroutines	59
Sample problem 10.....	53	Subroutines OFILE and TITLE	59
Aquifer of infinite width and height with finite-width and finite-height solute source	53	Graphics subroutines	59
Governing equation	53	Subroutines PLOT1D, PLOT2D, PLOT3D, and CNTOUR.....	59
Analytical solution	53	Running the programs.....	60
Description of program PATCHI.....	55	Array dimensions	60
Main program	55	Compiling and loading	60
Subroutine CNRMLI	55	Summary	61
Sample problem 11.....	57	References cited	61
Description of subroutines.....	57	Attachment 1.—Derivation of selected analytical solutions.....	63
Mathematical subroutines.....	57	Attachment 2—Program source-code listings.....	81
Subroutines EXERFC and GLQPTS	57	Attachment 3—Subroutine listing and data file GLQ.PTS.....	135
		Attachment 4—Program output for selected sample problems	163

FIGURES

	Page
1. Graph showing typical shape of equilibrium adsorption isotherm	5
2. Diagrams showing examples of situations in which the principle of superposition can be applied	9
3. Diagrams showing two examples of contaminant movement in field settings that can be simulated as one-dimensional solute-transport systems	11
4–6. Representations showing sample input data set and computer plot of concentration profiles generated by the program FINITE for a:	
4. Conservative solute in a finite-length system with first-type source boundary condition after 2.5, 5, 10, 15, and 20 hours.....	15
5. Solute subject to linear adsorption in a finite-length system with first-type source boundary condition after 20, 50, 100, and 150 hours	16
6. Conservative solute in a finite-length system with third-type source boundary condition after 2.5, 5, 10, 15, and 20 hours.....	19
7–9. Representations showing sample input data set and computer plot of concentration profiles generated by the program SEMINF for a:	
7. Conservative solute in a semi-infinite system with first-type source boundary condition after 2.5, 5, 10, 15, and 20 hours.....	22
8. Solute subject to first-order decay and linear equilibrium adsorption in a semi-infinite system with first-type source boundary condition after 20, 50, 100, and 150 hours.....	23
9. Conservative solute in a semi-infinite system with third-type source boundary condition after 2.5, 5, 10, 15, and 20 hours.....	25
10. Diagrams depicting plan view and vertical section of idealized two-dimensional solute transport in an aquifer of semi-infinite length and finite width, and plan view of idealized two-dimensional solute transport in an aquifer of semi-infinite length and infinite width.....	28
11. Diagram depicting plan view of a semi-infinite aquifer of infinite width showing location of waste-disposal pond and monitoring wells, and graph of observed solute concentration values and gaussian curve used to approximate concentration distribution at $x=0$	29
12–14. Representations showing sample input data set and computer plot of normalized concentration contours generated by the program:	
12. POINT2 for a conservative solute injected continuously into an aquifer of infinite areal extent after 25 and 100 days.....	32
13. STRIPF for a conservative solute in an aquifer of finite width with finite-width solute source after 1,500 and 3,000 days	35
14. STRIPI for a conservative solute in an aquifer of infinite width with finite-width solute source after 1,826 days.....	39
15. Histogram of normalized concentrations in relation to distance for the waste-disposal site in sample problem 8a and fitted gaussian distribution	43
16, 17. Representations showing sample input data set and computer plot of normalized concentration contours generated by the program GAUSS for a:	
16. Conservative solute in an aquifer of infinite width having a gaussian concentration distribution ($\sigma=150$ feet) at the inflow boundary at 300 days	44

	Page
17. Conservative solute in an aquifer of infinite width having a gaussian concentration distribution ($\sigma=65$ feet) at the inflow boundary at 300 days	45
18. Diagrams showing plan view and vertical section of idealized three-dimensional transport in an aquifer of semi-infinite length and finite width and height	46
19-21. Representations showing sample input data set and computer plot of normalized concentration contours generated by the program:	
19. POINT3 for a natural gradient tracer test in an aquifer of infinite extent after 400 days in the $z = 10$ -foot plane.....	50
20. PATCHF for a conservative solute in an aquifer of finite height and width after 3,000 days at heights of 75 and 50 feet above base of the aquifer	54
21. PATCHI for a solute subject to first-order chemical transformation in an aquifer of infinite height and width with solute source of finite height and width after 3,652.5 days at heights of 1,650, 1,700, and 1,750 feet above base of the aquifer	58

TABLES

	Page
1-6. Input data format for the program:	
1. FINITE	14
2. SEMINF	21
3. POINT2	30
4. STRIPF	34
5. STRIPI	37
6. GAUSS	41
7. Measured solute concentrations in monitoring wells downgradient from the waste-disposal site in sample problem 8b	42
8-10. Input data format for the program:	
8. POINT3	48
9. PATCHF	52
10. PATCHI	56

METRIC CONVERSION FACTORS

For readers who wish to convert measurements from the inch-pound system of units to the metric system of units, the conversion factors are listed below:

<i>Multiply inch-pound units</i>	<i>By</i>	<i>To obtain metric units</i>
inch (in)	25.4	millimeter (mm)
inch per hour (in/h)	25.4	millimeter per hour (mm/h)
foot (ft)	0.3048	meter (m)
foot per day (ft/d)	0.3048	meter per day (m/d)
gallon (gal)	0.003785	cubic meter (m ³)
square inch per hour (in ² /h)	6.4516	square centimeter per hour (cm ² /h)
foot squared per day (ft ² /d)	0.09290	meter squared per day (m ² /d)
cubic foot (ft ³)	0.02832	cubic meter (m ³)
cubic foot per day (ft ³ /d)	0.02832	cubic meter per day (m ³ /d)
pound per cubic foot (lb/ft ³)	0.01602	gram per cubic centimeter (g/cm ³)

 DEFINITION OF SYMBOLS

<i>Symbol</i>	<i>Dimension</i>	<i>Definitions</i>
C	M/L ³	Volumetric concentration
C _o	M/L ³	Specified concentration value along a boundary
CEC	1/M	Cation exchange capacity
D	L ² /T	Coefficient of hydrodynamic dispersion for one-dimensional solute transport
$\underline{\underline{D}}$	L ² /T	Hydrodynamic dispersion tensor in an isotropic system
$\underline{\underline{D}}_d$	L ² /T	Molecular diffusion tensor
$\underline{\underline{D}}_m$	L ² /T	Mechanical dispersion tensor
D*	L ² /T	Dispersion coefficient divided by the retardation factor, R
D _x , D _y , D _z	L ² /T	Magnitudes of the hydrodynamic dispersion tensor in a system having uniform flow
erf	—	Error function
erfc	—	Complimentary error function
exp	—	Exponential
h	L	Head
\vec{J}	M/L ² T	Solute flux due to dispersion or diffusion
k	L ³ /M	Slope of the linear equilibrium adsorption isotherm
k _d	L ³ /M	Distribution coefficient
$\underline{\underline{K}}$	L/T	Hydraulic conductivity tensor
K _s	—	Selectivity coefficient for ion exchange reactions
K _o	—	Modified Bessel function of second kind and zero order
n	—	Effective porosity
p	M/LT ²	Fluid pressure
P	—	Column Peclet number
R	—	Retardation factor for adsorbed solute
S	—	Mass concentration of adsorbed solute
t	T	Time
T	—	Number of displaced pore volumes
T _{1/2}	T	Half-life of radioactive solute
v	L/T	Magnitude of the average interstitial fluid velocity
v _x , v _y , v _z	L/T	Magnitudes of the average interstitial velocity components
$\underline{\underline{V}}$	L/T	Magnitude of uniform velocity
\bar{V}	L/T	Average interstitial fluid velocity
V*	L/T	Average interstitial fluid velocity divided by the retardation factor, R
z	L	Elevation head
α _l	L	Longitudinal dispersivity
α _t	L	Transverse dispersivity
γ	M/L ² T ²	Specific weight of water
θ	—	Soil moisture content (equal to porosity for saturated soils)
λ	1/T	First-order chemical transformation rate
ρ	M/L ³	Density of water
ρ _b	M/L ³	Bulk density of aquifer material
Σ	—	Summation
∞	—	Infinity
$\vec{\nabla}$	—	Gradient operator
∂	—	Partial derivative

ANALYTICAL SOLUTIONS FOR ONE-, TWO-, AND THREE-DIMENSIONAL SOLUTE TRANSPORT IN GROUND-WATER SYSTEMS WITH UNIFORM FLOW

By Eliezer J. Wexler

Abstract

Analytical solutions to the advective-dispersive solute-transport equation are useful in predicting the fate of solutes in ground water. Analytical solutions compiled from available literature or derived by the author are presented for a variety of boundary condition types and solute-source configurations in one-, two-, and three-dimensional systems having uniform ground-water flow. A set of user-oriented computer programs was created to evaluate these solutions and to display the results in tabular and computer-graphics format. These programs incorporate many features that enhance their accuracy, ease of use, and versatility. Documentation for the programs describes their operation and required input data, and presents the results of sample problems. Derivations of selected solutions, source codes for the computer programs, and samples of program input and output also are included.

Introduction

Contamination of ground water by inorganic and organic chemicals has become an increasing concern in recent years. These chemicals enter the ground-water system by a wide variety of mechanisms, including accidental spills, land disposal of domestic and industrial waste, and application of agricultural fertilizers and pesticides. Once introduced into an aquifer, these solutes will be transported by flowing ground water and may degrade water quality at nearby wells and streams.

To improve management and protection of ground-water resources, it is important to first understand the physical, chemical, and biological processes that control the transport of solutes in ground water. Predictions of the fate of ground-water contaminants can then be made to assess the effect of these chemicals on local water resources and to evaluate the effectiveness of remedial actions.

Two physical processes that govern the movement of ground-water solutes are (1) advection, which describes the transport of solutes by the bulk motion

of flowing ground water (Freeze and Cherry, 1979), and (2) hydrodynamic dispersion, which describes the spread of solutes along and transverse to the direction of flow resulting from both mechanical mixing and molecular diffusion (Bear, 1979, p. 230). Chemical reactions, including those mediated by microorganisms or caused by interaction with aquifer material or other solutes, may also affect the concentration of the solute.

These processes have been described quantitatively by a partial differential equation referred to as the "advective-dispersive solute-transport equation." Solution of the equation yields the solute concentration as a function of time and distance from the contaminant source. To apply the equation to a particular ground-water contamination problem, data must be provided on the ground-water velocity, coefficients of hydrodynamic dispersion, rates of chemical reactions, initial concentrations of solutes in the aquifer, configuration of the solute source, and boundary conditions along the physical boundaries of the ground-water flow system.

In ground-water systems having irregular geometry and nonuniform aquifer properties, numerical techniques are used to determine approximate solutions to the solute-transport equation. In aquifers having simple flow systems and relatively uniform hydrologic properties, analytical solutions, which represent exact mathematical solutions to the solute-transport equation, have been used to predict contaminant migration. These solutions are also used extensively in analysis of data from soil-column experiments and field tracer tests to determine aquifer properties, and have been used to verify the soundness of numerical models. In complex hydrogeologic systems, analytical solutions can still be useful to the hydrologist because they can provide estimates of

rates of solute spread and, thus, guide data collection and water-quality-monitoring efforts.

Although deriving an analytical solution for the solute-transport equation requires knowledge of higher mathematics, analytical solutions have already been derived and published for many combinations of solute-source configurations and boundary-condition types. After the solutions have been derived, they can be evaluated easily using electronic calculators or digital computers.

Purpose and scope

This report briefly describes the theoretical background of solute transport in a porous medium and then presents analytical solutions to the advective-dispersive solute-transport equation for a variety of aquifer and solute-source configurations and boundary conditions in systems having uniform (unidirectional) ground-water flow. Solutions for one-dimensional solute transport were compiled from various journals and reports, many of which are not readily available. Many of the solutions for two- and three-dimensional solute transport were modified from those presented in a report by Cleary and Ungs (1978), whereas others were derived by the author using integral transform techniques. (Detailed derivations of these solutions are provided in attachment 1.) All solutions are given in a simplified format, together with information on important assumptions in their derivation and limitations to their use.

Simple computer programs, written in FORTRAN-77, have been provided for evaluation of the analytical solutions presented. The programs were designed for ease of use and for enhanced accuracy. Documentation for these programs includes descriptions of program operation and the input data required. Source codes and samples of program output are provided at the end of the report. Subroutines that allow for graphical display of the program output, created using DISS-PLA software, are also described. Computer-generated plots are presented within the report.

Previous studies

Analytical solutions for the one-dimensional form of the solute-transport equation have appeared in reports and journals concerning physical chemistry, soil science, and water resources. These solutions, generally determined through Laplace transform techniques, have been applied to studies of solute movement in laboratory columns, unsaturated soils, and natural-gradient tracer tests. Solutions to the one-dimensional solute-transport equation for most

combinations of boundary and initial conditions are given in van Genuchten and Alves (1982); some of the more useful solutions appear in this report. Other sources that list several analytical solutions include Gershon and Nir (1969), Bear (1972), and Bear (1979).

Fewer analytical solutions have been published for the two- and three-dimensional forms of the solute-transport equation. Cleary and Ungs (1978) give several solutions derived using integral transform techniques, and Yeh (1981) presents a computer program that evaluates Green's function to model one-, two-, and three-dimensional transport.

Acknowledgments

This report was prepared at the request of Thomas E. Reilly of the U.S. Geological Survey, Office of Ground Water, in Reston, Va., who recognized the need for a compilation of analytical solutions to the transport equation. Thanks are extended to Robert Cleary, formerly of Princeton University, and Edward Sudicky of the University of Waterloo, Ontario, Canada, for introducing the author to the application of analytical solutions to the analysis of water-quality problems. Thanks are also extended to Mary Hill, Daniel J. Goode and Stephen P. Garabedian of the U.S. Geological Survey for their comments on an earlier version of this report.

Theoretical Background

Most models that simulate migration of dissolved contaminants in ground water solve the advective-dispersive solute-transport equation. This partial differential equation is derived from the conservation-of-mass principle (continuity equation), whereby the net rate of change of solute mass within a volume of porous media is equal to the difference between the flux of solute into and out of the volume, adjusted for the loss or gain of solute mass due to chemical reactions (Freeze and Cherry, 1979). The flux of solute into the volume is controlled by two physical processes—advection and hydrodynamic dispersion. Hydrodynamic dispersion, in turn, represents the combined effects of two other physical processes—molecular diffusion and mechanical dispersion.

Advection

Advective transport describes the bulk movement of solute particles along the mean direction of fluid flow at a rate equal to the average interstitial fluid velocity. In a saturated medium, this velocity can be calculated from Darcy's law, such that

$$\vec{v} = -\frac{\bar{K}}{n} \cdot \vec{\nabla}h, \quad (1)$$

where

- \vec{v} = average interstitial fluid velocity [L/T],
- \bar{K} = hydraulic conductivity tensor for medium [L/T],
- n = effective porosity [dimensionless], and
- $\vec{\nabla}h$ = gradient in head [dimensionless] (equal to dh/dx , the change in head per unit distance along the x-axis for uniform flow along the x-axis).

Head, h in equation 1, is equal to the sum of the elevation head, z , with respect to a datum level, and the pressure head, p/γ , where p is the fluid pressure (gage pressure) and γ is the specific weight of water (Bear, 1979, p. 62). Water flows from areas of higher head toward areas of lower head. Effective porosity, n , differs from total porosity (volume of pore space per unit volume of aquifer material) in that it does not include pores that are too small to transmit water or "dead-end" pores, those that are not interconnected with other pores.

In unsaturated porous media, the average interstitial fluid velocity can be approximated (Bear, 1979, p. 209) as

$$\vec{v} = -\frac{\bar{K}(\theta)}{\theta} \cdot \vec{\nabla}h, \quad (2)$$

where

- \vec{v} = average interstitial fluid velocity [L/T],
 - $\bar{K}(\theta)$ = unsaturated hydraulic conductivity tensor for medium, which is a function of moisture content [L/T], and
 - θ = moisture content of soil [dimensionless].
- This form of the equation assumes that the movement of air in the soil is negligible and that the density of water is constant.

Molecular diffusion

In addition to advective transport, solutes spread within the fluid in the porous medium by molecular diffusion. Diffusion results from the random collision of solute molecules and produces a flux of solute particles from areas of higher to lower solute concentration (Bear, 1979). The solute flux, \vec{J} , can be given by Fick's first law as

$$\vec{J} = \theta \bar{D}_d \cdot \vec{\nabla}C, \quad (3a)$$

where

- \bar{D}_d = second-rank diagonal tensor of molecular diffusion [L^2/T],
- $\vec{\nabla}C$ = concentration gradient [M/L^4], and
- C = concentration of solute (mass of solute per unit volume of fluid) [M/L^3].

Bear and Bachmat (1967) state that the coefficients of molecular diffusion in an isotropic medium are dependent on the diffusion coefficient of the particular solute in water and the tortuosity of the medium. Rates of molecular diffusion are independent of ground-water velocity, and diffusion occurs even in the absence of fluid movement.

Mechanical dispersion

The average interstitial fluid velocity represents a mathematical approximation. True velocities at points in the aquifer will differ from this average value, in both magnitude and direction. Local variations in ground-water velocity may not greatly affect the bulk movement of ground water, but they do control the fate of solute particles.

Mechanical dispersion describes the mixing and spreading of solutes along and transverse to the direction of flow in response to local variations in interstitial fluid velocities. On a microscopic scale (the scale of individual pores), mechanical dispersion results from (1) the distribution of velocities within an individual pore due to friction effects along the surface of soil grains, (2) differences in size of pores, (3) differences in path length for individual solute particles, and (4) the effect of converging and diverging flow paths (Freeze and Cherry, 1979, p. 75). On a larger (macroscopic) scale, mechanical dispersion results from local variations in hydraulic conductivity, and thus fluid velocity, owing to the heterogeneity of aquifer material (Bear, 1979, p. 229).

Laboratory tests on soil columns have shown that the flux of solutes due to mechanical dispersion can also be described using Fick's first law, as

$$\vec{J} = -\theta \bar{D}_m \cdot \vec{\nabla}C, \quad (3b)$$

where \bar{D}_m is the second-rank symmetric tensor of mechanical dispersion [L^2/T].

Scheidegger (1961) stated that the coefficients of mechanical dispersion can be related to the average interstitial fluid velocity by means of the geometric dispersivity of the medium. For a saturated porous medium, geometric dispersivity depends on hydraulic conductivity, length of a characteristic flow path, and tortuosity (Bear, 1972, p. 614). In a medium that is isotropic with respect to dispersion, geometric dispersivity can be expressed in terms of just two coefficients—longitudinal dispersivity, α_l , and transverse dispersivity, α_t (Bear, 1979, p. 234).

The elements of the mechanical dispersion tensor can be expressed in terms of longitudinal and transverse dispersivities, the magnitude of the velocity

vector, v , and the magnitudes of its components, v_x , v_y , and v_z (Bear, 1979, p. 235) as

$$\begin{aligned} D_{m_{xx}} &= [\alpha_1 v_x^2 + \alpha_t (v_y^2 + v_z^2)]/v \\ D_{m_{yy}} &= [\alpha_1 v_y^2 + \alpha_t (v_x^2 + v_z^2)]/v \\ D_{m_{xy}} &= D_{m_{yx}} = (\alpha_1 - \alpha_t) v_x v_y / v \\ D_{m_{yz}} &= D_{m_{zy}} = (\alpha_1 - \alpha_t) v_y v_z / v \\ D_{m_{xz}} &= D_{m_{zx}} = (\alpha_1 - \alpha_t) v_x v_z / v \\ D_{m_{zz}} &= [\alpha_1 v_z^2 + \alpha_t (v_x^2 + v_y^2)]/v. \end{aligned} \quad (4)$$

If a coordinate system is chosen, such that the direction of the average ground-water velocity is aligned with the x-direction ($v = v_x$ and $v_y = v_z = 0$), the off-diagonal terms in the dispersion tensor (eq. 4) will equal zero, and the mechanical dispersion tensor can be simplified to

$$\begin{aligned} D_{m_x} &= D_{m_{xx}} = \alpha_1 v \\ D_{m_y} &= D_{m_{yy}} = \alpha_t v \\ D_{m_z} &= D_{m_{zz}} = \alpha_t v. \end{aligned} \quad (5)$$

Hydrodynamic dispersion

As stated earlier, hydrodynamic dispersion is the flux of solute due to the combined effect of molecular diffusion and mechanical dispersion. Solute flux, \vec{J} , is given by Fick's first law as

$$\vec{J} = -\bar{D} \cdot \vec{\nabla} C, \quad (6)$$

where \bar{D} is the hydrodynamic dispersion tensor.

In a flow system having uniform flow aligned with the x-axis, the coefficients of the hydrodynamic dispersion tensor, D_x , D_y , and D_z , are given by

$$\begin{aligned} D_x &= D_{m_x} + D_d = \alpha_1 v + D_d \\ D_y &= D_{m_y} + D_d = \alpha_t v + D_d \\ D_z &= D_{m_z} + D_d = \alpha_t v + D_d. \end{aligned} \quad (7)$$

The effects of mechanical dispersion generally are much greater than those of molecular diffusion, and, except at low ground-water velocities, the contribution of molecular diffusion often is negligible.

In laboratory experiments using homogeneous materials, values for longitudinal dispersivity, α_1 , are typically between 0.004 and 0.4 inch (in), whereas in field studies, longitudinal dispersivities of as much as 328 feet (ft) have been determined (Freeze and Cherry, 1979). The larger field values can be attributed to increased mixing due to local variations in hydraulic conductivity (macrodispersion). A discussion of the apparent scale dependency of hydrodynamic dispersion is given in Anderson (1984). Trans-

verse dispersivity is generally less than longitudinal dispersivity, by a factor of 5 to 20 (Freeze and Cherry, 1979, p. 400).

Advective-dispersive solute-transport equation

The advective-dispersive solute-transport equation describes the time rate of change of solute concentration for a single solute and can be written as

$$\frac{\partial \theta C}{\partial t} = -\vec{\nabla} \cdot [\theta \vec{v} C - \theta \bar{D} \cdot \vec{\nabla} C] + \theta Q_s, \quad (8)$$

where Q_s is used to represent a general source or sink term for production or loss of solute within the system.

Equation 8 (after Bear, 1979, p. 241) can be written in terms of volumetric rather than mass concentrations because the fluid density is assumed to be constant. This is usually valid for most ground-water flow systems in which solutes are present in relatively low concentrations.

The analytical solutions presented in this report are derived for idealized systems in which the ground-water velocity is assumed to be uniform, aligned with the x-axis, and of constant magnitude. The moisture content (equal to porosity for saturated material) and the coefficients of hydrodynamic dispersion (see eq. 7) are also assumed to be constant. Given these assumptions, the three-dimensional form of the solute-transport equation for a uniform flow system can be expressed as

$$\frac{\partial C}{\partial t} = D_x \frac{\partial^2 C}{\partial x^2} + D_y \frac{\partial^2 C}{\partial y^2} + D_z \frac{\partial^2 C}{\partial z^2} - V \frac{\partial C}{\partial x} + Q_s, \quad (9)$$

where V represents the uniform velocity aligned with the x-axis.

In a thin aquifer in which the solute is uniformly mixed in the vertical (y-z) plane at the inflow boundary, the concentration gradient in the z-direction, $\partial C / \partial z$, equals zero. The two-dimensional solute-transport equation can be expressed as

$$\frac{\partial C}{\partial t} = D_x \frac{\partial^2 C}{\partial x^2} + D_y \frac{\partial^2 C}{\partial x^2} - V \frac{\partial C}{\partial x} + Q_s. \quad (10)$$

Finally, if the solute concentration is uniform over the entire inflow boundary, such as in a soil column, the term $\partial C / \partial y$ would also equal zero, yielding the one-dimensional solute-transport equation that can be expressed as

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} - V \frac{\partial C}{\partial x} + Q_s, \quad (11)$$

where D represents the dispersion coefficient along the direction of flow.

Chemical transformation

In addition to physical mechanisms that govern the movement of solutes through the ground-water system, chemical transformations may alter the concentration of a contaminant species in solution. Possible chemical transformations include dissolution, precipitation, oxidation, reduction, biological degradation, radioactive decay, and adsorption and ion-exchange reactions between the solute and the solid matrix of the aquifer.

If the processes involved in chemical transformation can be described mathematically, they then can be incorporated in the source term, Q_s , in the solute-transport equation for each chemical species. The analytical solutions described herein have been derived for systems in which the chemical transformation terms are given by first-order (linear) relations. The relations and their incorporation in the solute-transport equation are described below.

Linear equilibrium adsorption

Many ionic inorganic solutes and nonpolar organic solutes can be removed from solution by adsorption onto the surface of soil particles. The solute may be attracted to soil surfaces by either electrical attraction, Van der Waals forces, or chemical bonding (chemisorption). A general expression for the change in solute concentration due to partitioning of solute particles on the solid matrix (in the absence of dispersive or advective fluxes) can be stated as

$$\theta \frac{\partial C}{\partial t} = -\rho_b \frac{\partial S}{\partial t}, \quad (12)$$

where

ρ_b = bulk density of solid matrix measured as mass per unit volume of aquifer material [M/L^3], and
 S = mass of solute adsorbed on solid matrix per unit mass of solid material [dimensionless].

The amount of solute remaining in solution depends on the amount of solute in the adsorbed phase. The functional relation is usually determined experimentally through a series of batch tests in which solutions of known initial concentration are mixed with differing amounts of adsorbate. After equilibrium is achieved, the final solute concentration of each solution is measured, and the mass of solute adsorbed is calculated. An equilibrium adsorption curve can then be fitted to these data. Equilibrium concentrations are dependent on temperature, and the adsorption curve at a partic-

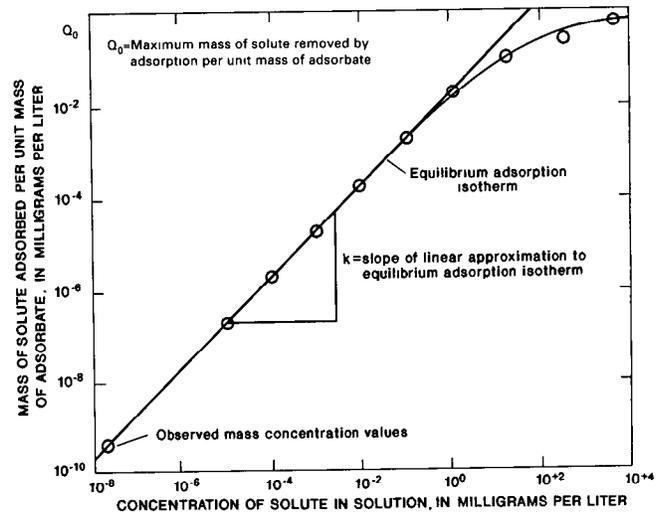


Figure 1.—Typical shape of equilibrium adsorption isotherm.

ular temperature is termed an “equilibrium adsorption isotherm.” A typical equilibrium adsorption isotherm is shown in figure 1.

A linear approximation of the equilibrium adsorption isotherm is generally applicable in systems in which the solute concentration is low relative to the adsorptive capacity of the porous medium. The adsorption of various nonionic organic solutes at trace concentrations onto sediments and soils has also been shown to be linear (Cherry and others, 1984). Many nonlinear forms for the adsorption isotherm, some empirical and some that account for the physical mechanisms of adsorption, are suggested in the literature (see Helfferich, 1962). However, the transport equation that incorporates these other forms must be solved by numerical methods.

Because the amount adsorbed depends solely on the solute concentration, equation 12 can be expressed as

$$\theta \frac{\partial C}{\partial t} = -\rho_b \frac{\partial S}{\partial C} \frac{\partial C}{\partial t}, \quad (13)$$

where $\partial S/\partial C$ is determined from the functional relation between C and S . For a linear equilibrium adsorption isotherm, $\partial S/\partial C$ is equal to the slope of the adsorption isotherm and often is termed k or the “partitioning coefficient.” The source term can be incorporated in the general three-dimensional form of the solute-transport equation (eq. 9) to yield

$$R \frac{\partial C}{\partial t} = D_x \frac{\partial^2 C}{\partial x^2} + D_y \frac{\partial^2 C}{\partial y^2} + D_z \frac{\partial^2 C}{\partial z^2} - V \frac{\partial C}{\partial x}, \quad (14)$$

where R is referred to as the “retardation factor,” given by

$$R = 1 + \frac{k\rho_b}{\theta}. \quad (15)$$

Dividing through by R yields

$$\frac{\partial C}{\partial t} = D_x^* \frac{\partial^2 C}{\partial x^2} + D_y^* \frac{\partial^2 C}{\partial y^2} + D_z^* \frac{\partial^2 C}{\partial z^2} - V^* \frac{\partial C}{\partial x}, \quad (16)$$

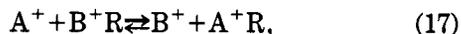
where V^* and D_x^* , D_y^* , and D_z^* are the scaled (or retarded) velocity and dispersion coefficients, respectively. Equation 16 shows that transport of solutes subject to linear adsorption can be simulated in the same manner as a nonadsorbed solute using these scaled coefficients. Because the apparent velocity of the adsorbed solute is reduced, the solute will arrive at a given point later than a nonadsorbed solute.

The use of equilibrium isotherms assumes that equilibrium exists at all times between the porous medium and the solute in solution. This assumption is generally valid when the adsorption process is fast in relation to the ground-water velocity (Cherry and others, 1984). If adsorption proceeds slowly, kinetics of the reaction must be considered. Nonequilibrium adsorption relations can be incorporated in the transport equation, but numerical methods are needed for solution of the resulting equation.

The process of adsorption is also assumed to be reversible. If hysteresis effects during desorption are significant, other forms of the adsorption isotherms must be considered, and numerical methods would be required.

Ion exchange

Ion exchange is an adsorption process in which a cation in solution replaces another cation that is electrically bound to colloidal material in the soil. Under certain conditions, ion exchange can be modeled in a manner similar to linear adsorption (R.W. Cleary, Princeton University, written commun., 1977). The exchange reaction for monovalent ions can be expressed as



where A^+ is used to represent a cation in solution, R is the exchange medium, and B^+ represents the counter ion released from the exchanger. At equilibrium, a selectivity coefficient, K_s , can be defined, such that

$$K_s = \frac{[B^+][A^+R]}{[A^+][B^+R]}, \quad (18)$$

where the bracketed terms represent the activities of each constituent.

Measured values of K_s can be used in simulating transport by making the following assumptions: (1) if all exchange sites are assumed to be occupied initially,

then $[B^+R]$ represents the total cation exchange capacity (CEC) of the medium, which can be determined experimentally and then treated as a constant; (2) the counter ion, B^+ , is usually present in solution at much greater concentrations than the solute A^+ , and releases of additional amounts of the counter ion by exchange will not significantly alter its concentration; thus, $[B^+]$ can also be treated as a constant; and (3) the relation between the amount of solute on the exchange sites and the amount remaining in solution can be defined as

$$k_d = \frac{[A^+]}{[A^+R]}, \quad (19)$$

where the distribution coefficient, k_d , is determined through laboratory batch tests.

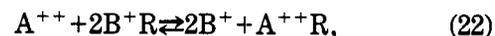
Given these assumptions, the general expression for the change in solute concentration due to cation exchange can be expressed as

$$\theta \frac{\partial C}{\partial t} = -\rho_b k_d \frac{\partial C}{\partial t}, \quad (20)$$

where

$$k_d = \frac{K_s \cdot \text{CEC}}{[B^+]}. \quad (21)$$

This term would replace k in equation 15. For monovalent-divalent cation exchange, where



the distribution coefficient can be given by

$$k_d = \frac{K_s \cdot \text{CEC}^2}{[B^+]^2}. \quad (23)$$

First-order chemical reactions

Simple chemical reaction terms can be formulated to account for the kinetics of reactions under nonequilibrium conditions. A first-order chemical process, such as radioactive decay or biological degradation, involves the irreversible unimolecular conversion of solute A to solute B ($A \rightarrow B$). The rate of the reaction can be given by

$$\frac{d[A]}{dt} = -\lambda[A], \quad (24)$$

where λ is the rate coefficient [$1/T$]. The rate coefficient can be expressed in terms of the half-life of the solute, $T_{1/2}$ (the time required for the concentration of the solute species to be reduced to half the initial concentration), as

$$\lambda = \ln(2)/T_{1/2} = 0.693/T_{1/2}. \quad (25)$$

Equation 9 can be written to incorporate the first-order reaction as

$$\frac{\partial C}{\partial t} = D_x \frac{\partial^2 C}{\partial x^2} + D_y \frac{\partial^2 C}{\partial y^2} + D_z \frac{\partial^2 C}{\partial z^2} - V \frac{\partial C}{\partial x} - \lambda C. \quad (26)$$

If the solute is subject to linear adsorption and to first-order chemical transformation in both the solute and adsorbed phases, equation 9 can be expressed as

$$R \frac{\partial C}{\partial t} = D_x \frac{\partial^2 C}{\partial x^2} + D_y \frac{\partial^2 C}{\partial y^2} + D_z \frac{\partial^2 C}{\partial z^2} - V \frac{\partial C}{\partial x} - R\lambda C \quad (27)$$

where R is the retardation factor (eq. 15) or

$$\frac{\partial C}{\partial t} = D_x^* \frac{\partial^2 C}{\partial x^2} + D_y^* \frac{\partial^2 C}{\partial y^2} + D_z^* \frac{\partial^2 C}{\partial z^2} - V^* \frac{\partial C}{\partial x} - \lambda C, \quad (28)$$

where V^* and D^* represent the scaled velocity and dispersion coefficients. If the adsorbed phase is not subject to chemical transformation, λ in equation 28 should be replaced by λ^* , where

$$\lambda^* = \lambda/R. \quad (29)$$

Some multiple-ion reactions can be approximated as a first-order reaction if all ions, except the species being considered, are present at high concentrations (R.W. Cleary, Princeton University, written commun., 1977). For example, if the reaction involves the conversion of solutes A and B to form solute C ($A+B \rightarrow C$), the rate of reaction would be given as

$$\frac{d[A]}{dt} = -\lambda_{AB}[A][B]. \quad (30)$$

If solute B is present at high concentration, its concentration will not change significantly due to conversion of A and [B] can be treated as a constant. Equation 26 or 28 can then be used with a modified λ term, where $\lambda = \lambda_{AB}[B]$. General bimolecular or multiple-ion reactions result in nonlinear chemical source terms. Reversible reactions and multistep reactions require simultaneous solution of the transport equation written for each species. Simulation of transport involving these chemical processes usually requires numerical methods.

Initial conditions

To solve the solute-transport equation, a complete set of boundary and initial conditions must be specified. Initial conditions are used to define the solute concentration in the aquifer at the time inflow of solute begins. For the analytical solutions presented

in this report, the initial conditions are specified such that all initial concentrations are zero. If the solute is conservative, a constant initial background solute concentration can be added to the calculated concentrations. Analytical solutions for one-dimensional transport of nonconservative solute transport with nonzero initial concentrations are given in van Genuchten and Alves (1982).

Boundary conditions

Three types of boundary conditions are generally associated with the solute-transport equation. The first-type (or Dirichlet) boundary condition specifies the value of the concentration along a section of the flow-system boundary. The second-type (or Neumann) boundary condition specifies the gradient in solute concentration across a section of the boundary. The third-type (or Cauchy) boundary condition is applied where the flux of solute across the boundary is dependent on the difference between a specified concentration value on one side of the boundary and the solute concentration on the opposite side of the boundary. These three types of boundary conditions are used to describe conditions at the inflow and outflow ends of the flow system and also along the lateral boundaries of two- and three-dimensional systems.

Inflow boundary

The third-type boundary condition best describes solute concentrations at the inflow end in a uniform flow system (Bear, 1979, p. 268), where a well-mixed solute enters the system by advection across the boundary and is transported away from the boundary by advection and dispersion. The boundary conditions can be given as

$$VC - D_x \frac{\partial C}{\partial x} = VC_0, \quad x=0, \quad (31)$$

where C_0 is the known measured concentration in the influent water. The third-type boundary condition allows for solute concentration at the inflow boundary to be lower than C_0 initially and then to increase as more solute enters the system. Over time, the concentration gradient across the boundary, $\partial C/\partial x$, decreases as the concentration at the inflow boundary approaches C_0 .

Alternatively, a first-type boundary condition can be specified at the inflow end, such that

$$C = C_0, \quad x=0. \quad (32)$$

Application of this simpler form of boundary condition presumes that the concentration gradient across the

boundary equals zero as soon as flow begins. However, this may lead to overestimation of the mass of solute in the system at early times.

Equation 31 indicates that the difference between concentrations predicted for a system having a first-type source boundary condition and a system having a third-type boundary condition should decrease as the quantity D/V decreases. Additional discussions of the effect and relative merits of the different types of inflow boundary conditions are presented in Gershon and Nir (1969), van Genuchten and Alves (1982), and Parker and van Genuchten (1984).

Outflow boundary

Often, the outflow boundary of the system being simulated is far enough away from the solute source that the boundary will not affect solute concentrations within the area of interest. Such a system can be treated as being "semi-infinite," and either a first-type or second-type boundary condition can be specified as

$$C, \quad \frac{\partial C}{\partial x} = 0, \quad x = \infty. \quad (33)$$

When the system has a finite length, and solute concentrations near the outflow boundary are of interest, selection of an appropriate boundary condition becomes more difficult. In general, if the system discharges to a large, well-mixed reservoir and the additional solute will not significantly alter reservoir concentrations, then a third-type or first-type boundary condition (similar to the inflow boundary) can be used. If the reservoir is small or not well mixed, such as at the end of the soil column in figure 2A, concentrations in the reservoir would equal solute concentration at the discharge end of the system, and thus no concentration gradient would exist across the boundary. This can be specified by a second-type boundary condition as

$$\frac{\partial C}{\partial x} = 0, \quad x = L, \quad (34)$$

where L represents the length of the finite system.

Van Genuchten and Alves (1982, p. 90-96) analyzed the difference between predicted concentrations obtained using analytical solutions for a semi-infinite system and a finite system having a second-type boundary condition in terms of two dimensionless numbers: (1) the column Peclet number (P) and (2) the number of displaced pore volumes (T), which are defined by

$$P = \frac{VL}{D} \quad (35)$$

and

$$T = \frac{Vt}{L}. \quad (36)$$

They found that the predicted concentration at points near the outflow boundary begins to differ significantly for T greater than 0.25 and that the differences increase as T approaches 1 (corresponding to movement of the solute front closer to the outflow boundary). The magnitude of the difference and distance inward from the outflow boundary at which the solutions diverge decreases as P values increase.

Lateral boundaries

In two- and three-dimensional systems, impermeable or no-flow boundaries may be present at the base, top, or sides of the aquifer. Because there is no advective flux across the boundary, and molecular diffusion across the boundary is assumed to be negligible, the general third-type boundary condition simplifies to a second-type boundary condition, expressed as

$$\frac{\partial C}{\partial y} = 0, \quad y = 0 \text{ and } y = W \quad (37a)$$

and

$$\frac{\partial C}{\partial z} = 0, \quad z = 0 \text{ and } z = H \quad (37b)$$

where W and H represent the width and height of the aquifer, respectively.

In many cases, lateral boundaries of the system may be far enough away from the area of interest that the system can be treated as being infinite along the y - and z -axes. Boundary conditions can then be specified as

$$C, \quad \frac{\partial C}{\partial y} = 0, \quad y = \pm \infty \quad (38a)$$

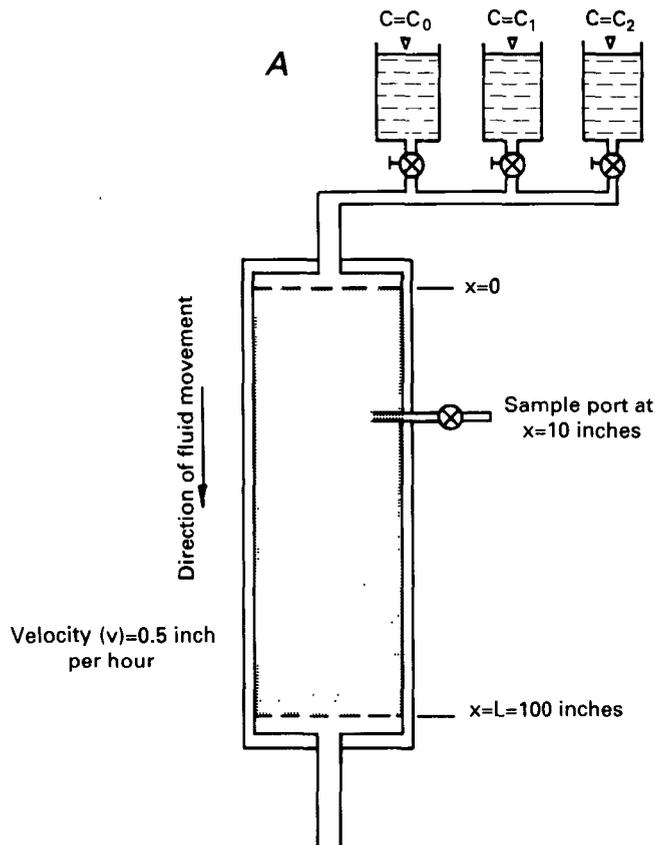
and

$$C, \quad \frac{\partial C}{\partial z} = 0, \quad z = \pm \infty. \quad (38b)$$

Superposition

Because the solute-transport equation is a linear partial-differential equation, the principle of superposition can be used to calculate concentrations in the system if solute concentrations at the inflow boundary vary over time. The general form of the solution can be expressed as

$$C = C_0 \cdot A(x, y, z, t) + (C_1 - C_0) \cdot A(x, y, z[t - t_1]), \quad (39)$$



Solute concentration
 $C_0=100$ milligrams per liter
 $C_1=300$ milligrams per liter
 $C_2=0.0$ milligram per liter

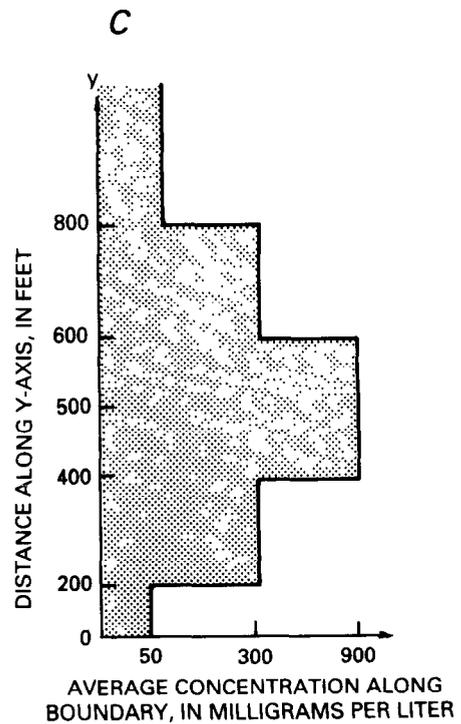
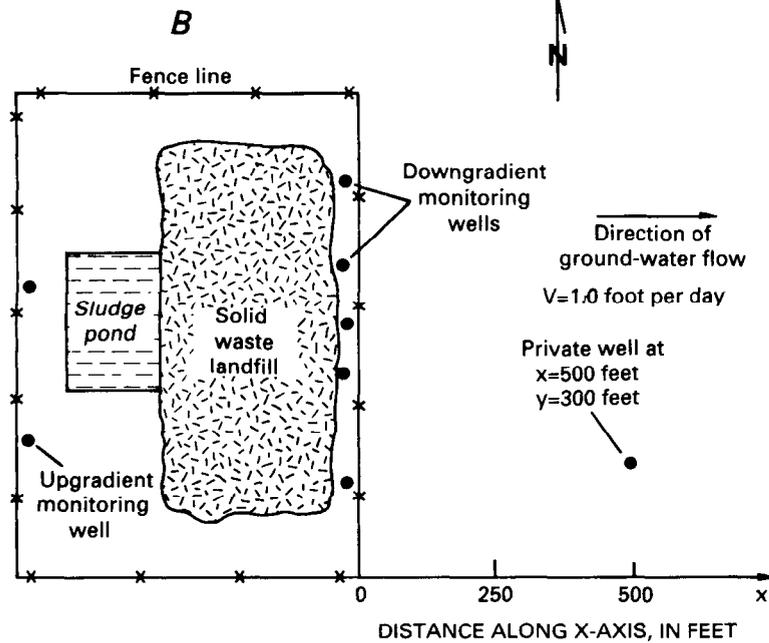


Figure 2.—Examples of situations in which the principle of superposition can be applied: A, soil column with time-varying input concentration (cases A and B in text), B, waste-disposal site with spatially varying input concentrations (case C in text), and C, plot of average concentration measured along waste-disposal site boundary.

where

- C_o = initial solute concentration at boundary,
 $A(x,y,z,t)$ = general form of analytical solution where concentration is a function of space and time,
 C_1 = solute concentration at boundary after $t=t_1$, and
 t_1 = time at which solute concentration changes at boundary.

The principle of superposition should be familiar to most hydrologists who have used analytical solutions (such as the Theis equation) in analyzing aquifer tests. Several examples are provided to illustrate its application to solute-transport simulation.

Case A:

A solution is passed through a 100-in-long soil column (fig. 2A) for a period of 10 hours, with $V=0.5$ inch per hour (in/h), $D=0.05$ square inch per hour (in²/h), and $C_o=100$ milligrams per liter (mg/L). At the end of the 10-hour period, the concentration of the influent is increased to $C_1=300$ mg/L. Of interest is the concentration at $x=10$ in at the end of a total elapsed time of 20 hours.

The analytical solution for transport of a conservative solute in a semi-infinite column (assuming that boundary effects at $x=L$ are negligible) with a first-type inflow boundary condition was given by Ogata and Banks (1961) as

$$A(x,t) = \frac{1}{2} \left\{ \operatorname{erfc} \left[\frac{x-Vt}{2\sqrt{Dt}} \right] + \exp \left[\frac{Vx}{D} \right] \cdot \operatorname{erfc} \left[\frac{x+Vt}{2\sqrt{Dt}} \right] \right\},$$

where erfc is the complementary error function. (The solution is described in more detail later.) For the values given, equation 39 becomes

$$\begin{aligned} C(10 \text{ in}, 20 \text{ hours}) &= 100 \text{ mg/L} \cdot A(10 \text{ in}, 20 \text{ hours}) + (300 \\ &\quad \text{mg/L} - 100 \text{ mg/L}) \cdot A(10 \text{ in}, [20 \\ &\quad \text{hours} - 10 \text{ hours}]) \\ &= 100 \text{ mg/L} \cdot (0.984) + 200 \text{ mg/L} \\ &\quad \cdot (0.088) \\ &= 116.0 \text{ mg/L}. \end{aligned}$$

Case B:

This case is similar to case A, except that at the end of 10 hours, solute-free water ($C_2=0.0$ mg/L) is passed through the soil column, thus creating a solute pulse of finite duration. The concentration of solute at $x=10$ in and $t=20$ hours can be given from equation 39 as

$$C(10 \text{ in}, 20 \text{ hours}) = 100 \text{ mg/L} \cdot A(10 \text{ in}, 20 \text{ hours}) + (0 - 100 \text{ mg/L}) \cdot A(10 \text{ in}, [20 - 10 \text{ hours}])$$

$$\begin{aligned} &= 100 \text{ mg/L} \cdot (0.984) - 100 \text{ mg/L} \\ &\quad \cdot (0.088) \\ &= 89.6 \text{ mg/L}. \end{aligned}$$

The principle of superposition can also be used to simulate more complex solute configurations at the boundary of two- and three-dimensional systems, as shown in case C. Also, if solute sources are at two locations, the calculated concentration from the first source at a particular point of interest can simply be added to the calculated concentration from the second source at that point.

Case C:

A waste-disposal site, shown in plan view in figure 2B, has a solid-waste landfill and a smaller area for sludge disposal. Measured concentrations in fully screened wells along the eastern boundary downgradient from the landfill had chloride concentrations averaging 300 mg/L. Wells downgradient from both the sludge pond and the landfill had concentrations averaging 900 mg/L. Background chloride concentrations are 50 mg/L. Given $V=1$ foot per day (ft/d), $D_x=20$ feet squared per day (ft²/d), and $D_y=4$ ft²/d, calculate the concentration at a private well located at $x=500$ ft and $y=300$ ft at the end of 1 year.

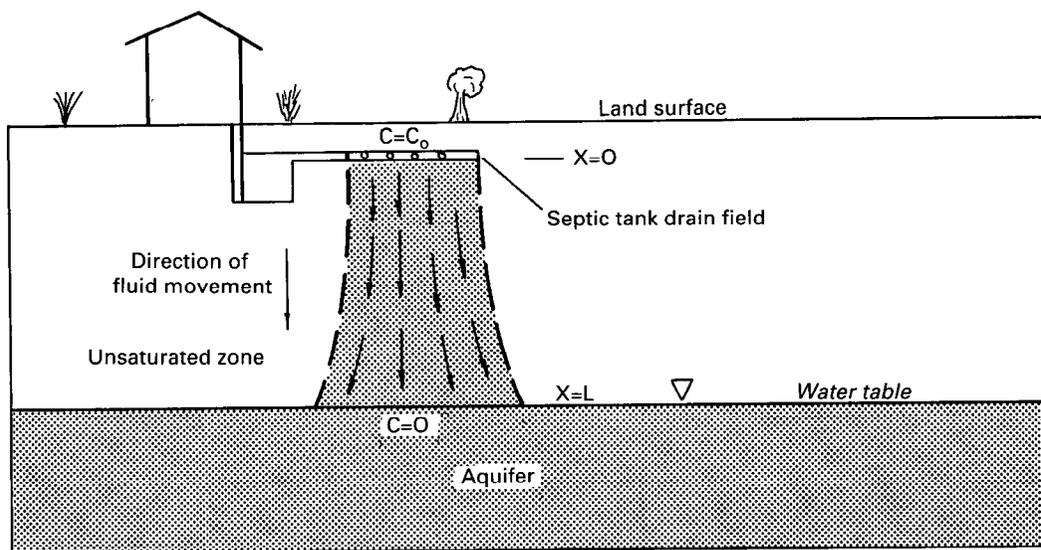
The analytical solution for transport of a conservative solute in an infinitely wide aquifer having a finite-width or "strip" source along the inflow boundary is modified from Cleary and Ungs (1978, p. 17):

$$\begin{aligned} A(x,y,Y_1,Y_2,t) &= \frac{x}{4\sqrt{\pi D_x}} \exp \left(\frac{Vx}{2D_x} \right) \int_0^t \tau^{-\frac{3}{2}} \\ &\quad \exp \left[\frac{-x^2}{4D_x\tau} - \frac{V^2\tau}{4D_x} \right] \cdot \left\{ \operatorname{erfc} \left[\frac{Y_1-y}{2\sqrt{D_y\tau}} \right] \right. \\ &\quad \left. - \operatorname{erfc} \left[\frac{Y_2-y}{2\sqrt{D_y\tau}} \right] \right\} d\tau, \end{aligned}$$

where Y_1 and Y_2 are coordinates of the endpoints of the source on the y -axis and τ is a dummy variable of integration. The solute source can be represented by two strip sources, the first extending from $Y_1=200$ to $Y_2=800$ ft, with an effective concentration, C_1 , of 250 mg/L (difference between measured and background concentration) and the second extending from $Y_1=400$ to $Y_2=600$ ft, with a concentration, C_2 , of 600 mg/L (measured concentration minus first-source effective concentration and background concentration). The concentration at the private well can be calculated as

$$C(500 \text{ ft}, 300 \text{ ft}) = C_{\text{background}} + C_1 \cdot A(500 \text{ ft}, 300 \text{ ft}, 200 \text{ ft}, 800 \text{ ft}, 365 \text{ days}) + C_2 \cdot A(500 \text{ ft}, 300 \text{ ft}, 400 \text{ ft}, 600 \text{ ft}, 365 \text{ days})$$

A



B

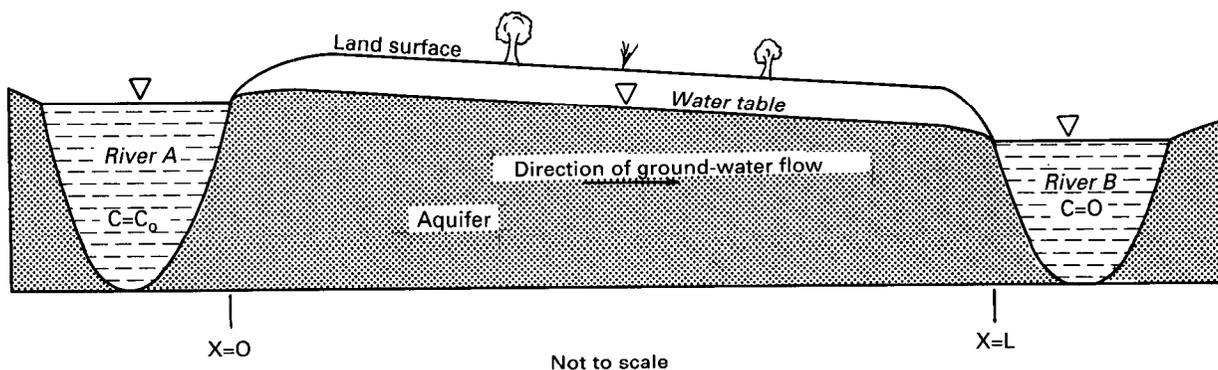


Figure 3.—Two examples (A and B) of contaminant movement in field settings that can be simulated as one-dimensional solute-transport systems.

$$=50 \text{ mg/L} + 250 \text{ mg/L} \cdot (0.1612) + 600 \text{ mg/L} \cdot (0.1354) = 171.5 \text{ mg/L}.$$

One-Dimensional Solute Transport

Many analytical solutions for the one-dimensional form of the solute-transport equation (eq. 11) were

developed for study of dispersion phenomena in soil or adsorption columns. Some field situations can also be idealized as one-dimensional transport systems; two examples are shown in figure 3. Figure 3A represents steady vertical flow through the unsaturated zone beneath a septic tank drain field. Transport at the center of the field is simulated, and the horizontal spread of solutes along the edges of the field is ignored. Figure 3B represents a case of steady hori-

zontal ground-water flow from river A, which has been contaminated, to river B.

One-dimensional systems can be finite, semi-infinite, or infinite in extent. In the finite or semi-infinite systems, water containing a known concentration of a contaminant species enters the system at the origin (at $x=0$). Water and solute exit at the opposite end of the system (at $x=L$), which could represent the water table, a stream, or the end of a soil column (fig. 3).

In the finite-length system, the outflow boundary is close enough that it will have an effect on the magnitude of concentrations within the area of interest. If the outflow boundary is far enough away as to have negligible effect on solute concentrations in the area of interest (equivalent to $T < 0.25$, where T is the number of displaced pore volumes), solutions for a semi-infinite system can be used and are generally easier to evaluate.

An example of transport in an infinite system might be the injection of a solute into the center of a long soil column. In this case, the spread of solute, both upgradient and downgradient from the source, is of interest. Solutions for an infinite system can be found in van Genuchten and Alves (1982) and Bear (1972, 1979).

For the four analytical solutions presented in this section, either a first- or third-type boundary condition is specified at the inflow end of a finite or semi-infinite system. Specifically, the solutions are for a

- Finite system with a first-type boundary condition at the inflow end,
- Finite system with a third-type boundary condition at the inflow end,
- Semi-infinite system with a first-type boundary condition at the inflow end, and
- Semi-infinite system with a third-type boundary condition at the inflow end.

Solutions for the finite systems assume a second-type boundary condition at the outflow end.

Two computer programs, FINITE and SEMINF, were developed to calculate concentrations in these four systems as a function of distance and elapsed time. These programs are also described in this section. The format used in presenting each of the solutions may seem repetitive, but it provides for easy reference.

Finite system with first-type source boundary condition

Governing equation

One-dimensional solute-transport equation:

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} - V \frac{\partial C}{\partial x} - \lambda C \quad (40)$$

Boundary conditions:

$$C = C_0, \quad x = 0 \quad (41)$$

$$\frac{\partial C}{\partial x} = 0, \quad x = L \quad (42)$$

Initial condition:

$$C = 0, \quad 0 < x < L \quad \text{at } t = 0 \quad (43)$$

Assumptions:

1. Fluid is of constant density and viscosity.
2. Solute may be subject to first-order chemical transformation (for a conservative solute, $\lambda = 0$).
3. Flow is in x -direction only, and velocity is constant.
4. The longitudinal dispersion coefficient (D), which is equivalent to D_x (eq. 7), is constant.

Analytical solution

The following equation is modified from van Genuchten and Alves (1982, p. 63–65):

$$C(x,t) = C_0 \left\{ \frac{\exp\left[\frac{(V-U)x}{2D}\right] + \frac{(U-V)}{(U+V)} \exp\left[\left(\frac{V+U}{2D}\right)x - \frac{UL}{D}\right]}{\left[1 + \frac{(U-V)}{(U+V)} \exp\left[\frac{-UL}{D}\right]\right]} - 2 \exp\left[\frac{Vx}{2D} - \lambda t - \frac{V^2 t}{4D}\right] \right. \\ \left. \cdot \sum_{i=1}^{\infty} \frac{\beta_i \sin\left(\frac{\beta_i x}{L}\right) \left[\beta_i^2 + \left(\frac{VL}{2D}\right)^2\right] \exp\left[-\frac{\beta_i^2 Dt}{L^2}\right]}{\left[\beta_i^2 + \left(\frac{VL}{2D}\right)^2 + \frac{VL}{2D}\right] \left[\beta_i^2 + \left(\frac{VL}{2D}\right)^2 + \frac{\lambda L^2}{D}\right]} \right\}, \quad (44)$$

where $U = \sqrt{V^2 + 4\lambda D}$ and β_i are the roots of the equation

$$\beta \cot \beta + \frac{VL}{2D} = 0. \quad (45)$$

Comments:

Values of the first six roots of equation 45, $a \cdot \cot(a) + c = 0$, are tabulated in Carslaw and Jaeger (1959, p. 492) for various values of the constant c . Additional roots of equation 45 can be found through standard root-search techniques.

The maximum number of terms that should be computed in the infinite series summation depends on

how fast the series converges. Convergence is usually a problem at early times (or at $T \ll 1$) near the origin ($x=0$), especially when the column Peclet number (P in eq. 35) is relatively large. The program described below determines that the series has converged if the absolute value of the last term in the series is less than 1×10^{-12} . A good initial estimate for the maximum number of terms is 100, but more should be used if the program indicates that the series did not converge. A minimum of 25 roots is used by the program.

For a solute that is not subject to first-order chemical transformation ($\lambda=0$), equation 44 can be replaced (Cleary and Adrian, 1973; Wexler and Cleary, 1979) by

$$C(x,t) = C_0 \left\{ 1 - 2 \exp \left[\frac{Vx}{2D} - \frac{V^2 t}{4D} \right] \cdot \sum_{i=1}^{\infty} \frac{\beta_i \sin \left(\frac{\beta_i x}{L} \right) \exp \left(-\frac{\beta_i^2 D t}{L^2} \right)}{\beta_i^2 + \left(\frac{VL}{2D} \right)^2 + \frac{VL}{2D}} \right\} \quad (46)$$

For large values of time (steady-state solution), equation 44 can be reduced (van Genuchten and Alves, 1982, p. 58) to

$$C(x) = C_0 \exp \frac{\left[\frac{(V-U)x}{2D} \right] + \frac{(U-V)}{(U+V)} \exp \left[\frac{(V+U)x}{2D} - \frac{UL}{D} \right]}{\left[1 + \frac{(U-V)}{(U+V)} \exp \left(-\frac{UL}{D} \right) \right]} \quad (47)$$

Linear equilibrium adsorption and ion exchange can be simulated by first dividing the coefficients D and V by the retardation factor, R (eq. 15). (Note: U in eqs. 44 and 47 would be given by $U = \sqrt{V^* + 4\lambda D^*}$). Temporal variations in source concentration can be simulated through the principle of superposition (eq. 39).

Description of program FINITE

The program FINITE computes the analytical solution to the one-dimensional solute-transport equation for a finite system with a first-type (eq. 44) or third-type (eq. 52) source boundary condition at the inflow end. It consists of a main program and four subroutines—ROOT1, ROOT3, CNRML1, and CNRML3. The function of the main program and subroutines ROOT1 and CNRML1 are outlined below; the program code listing is presented in attachment 2. Subroutines ROOT3 and CNRML3 are called when a third-type boundary condition is specified and are described in a subsequent section.

The program also calls the output subroutines TITLE, OFILE, and PLOT1D, which are common to most of the programs described in this report. These subroutines are described in detail later.

Main program

The main program reads and prints all input data needed to specify model variables. The required input data and the format used in preparing a data file are shown in table 1.

The program calls subroutine ROOT1 to compute the positive roots of equation 45 when a first-type source boundary condition is specified and then executes a set of nested loops. The inner loop calls subroutine CNRML1 to calculate the concentration for a particular time value and distance; the outer loop cycles through all specified time values and prints a table of concentration in relation to distance for each time value. Graphs of concentration in relation to distance can also be plotted.

Subroutines ROOT1 and CNRML1

Subroutine ROOT1 calculates the roots of the equation

$$a \cdot \cot(a) + c = 0$$

by an iterative procedure. The first root is known to lie between $\pi/2$ and π , and an initial estimate of 0.75π is made. Newton's second-order method (Salvadori and Baron, 1961, p. 6) is used to correct and update the estimate at each iteration. A maximum of 50 iterations and a convergence criterion of 1.0×10^{-10} are set in the subroutine. Each subsequent root of the equation is about π greater than the previous one. This value is used as an initial estimate in the search for the remaining roots.

Subroutine CNRML1 calculates the normalized concentration (C/C_0) for a particular time value and x -distance value, using equation 44 for a solute subject to first-order chemical transformation and equation 46 if the solute is conservative ($\lambda=0$). The number of terms taken in the infinite series summation is specified in the input data.

Sample problems 1a and 1b

Two sample problems are presented that use data similar to the data given in Lai and Jurinak (1972). In sample problem 1a, a conservative solute is introduced into a saturated soil column under steady flow. Model variables are

Velocity (V)	= 0.6 in/h
Longitudinal dispersion (D)	= 0.6 in ² /h
System length (L)	= 12 in

Table 1.—Input data format for the program FINITE

Data set	Columns	Format	Variable name	Description
1	1 - 60	A60	TITLE	Data to be printed in a title box on first page of program output. Last line in data set must have an "=" in column 1. First four lines are also used as title for plot.
2	1 - 4	I4	NBC	Boundary condition type (NBC = 1 for a first-type boundary condition; NBC = 3 for a third-type boundary condition).
	5 - 8	I4	NX	Number of x-coordinates at which solution will be evaluated.
	9 - 12	I4	NT	Number of time values at which solution will be evaluated.
	13 - 16	I4	NROOT	Number of terms used in infinite series summation.
	17 - 20	I4	IPLT	Plot control variable. Concentration profiles will be plotted if IPLT is greater than 0.
3	1 - 10	A10	CUNITS	Character variable used as label for units of concentration in program output.
	11 - 20	A10	VUNITS	Units of ground-water velocity.
	21 - 30	A10	DUNITS	Units of dispersion coefficient.
	31 - 40	A10	KUNITS	Units of solute-decay coefficient.
	41 - 50	A10	LUNITS	Units of length.
	51 - 60	A10	TUNITS	Units of time.
4	1 - 10	F10.0	CO	Solute concentration at inflow boundary.
	11 - 20	F10.0	VX	Ground-water velocity in x-direction. ¹
	21 - 30	F10.0	DX	Longitudinal dispersion coefficient. ¹
	31 - 40	F10.0	DK	First-order solute-decay coefficient. ¹
	41 - 50	F10.0	XL	Length of flow system. ¹
	51 - 60	F10.0	XSCLP	Scaling factor by which x-coordinate values are divided to convert them to plotter inches.
5	1 - 80	8F10.0	X(I)	X-coordinates at which solution will be evaluated (eight values per line).
6	1 - 80	8F10.0	T(I)	Time values at which solution will be evaluated (eight values per line).

¹All units must be consistent.

Solute concentration at inflow boundary (C₀) = 1.0 mg/L.

Retardation factor (R) = 8.31
 Scaled velocity (V*) = 0.072 in/h
 Scaled dispersion coefficient (D*) = 0.072 in²/h.

Concentrations are calculated for points 0.5 in apart at elapsed times of 2.5, 5, 10, 15, and 20 hours.

Concentrations are calculated for points 0.5 in apart at elapsed times of 20, 50, 100, and 150 hours.

In sample problem 1b, a solute is removed by linear equilibrium adsorption. Additional model variables are

The input data sets for sample problems 1a and 1b are shown in figures 4A and 5A; computer plots of concentration profiles generated by the program FINITE are shown in figures 4B and 5B. Comparison of the concentration profiles at 20 hours shows the retarding effect of adsorption on solute movement.

Soil bulk density (ρ_b) = 0.047 lb(mass)/in³
 Porosity (n) = 0.45
 Slope of adsorption isotherm (k) = 70 in³/lb (mass).

Program output for sample problem 1a is presented in attachment 4. Sample problems 1a and 1b each required 3.9 seconds (s) of central processing unit (CPU) time on a Prime model 9955 Mod II.

From these values and equations 15 and 16 (substituting n for θ), the terms obtained are

A

Sample Problem 1a -- Solute transport in a finite-length soil column with a first-type boundary condition at $x=0$
 Model Parameters: $L=12$ in, $V=0.6$ in/h, $D=0.6$ in²/h
 $K1=0.0$ per h, $C0=1.0$ mg/L

MG/L	25	05	50	1	PER HOUR	INCHES	HOURS		
1.0	0.6	0.6	0.6	0.6	0.0	12.0	1.2		
0.0	0.5	1.0	1.0	1.5	2.0	2.5	3.0	3.5	
4.0	4.5	5.0	5.5	6.0	6.5	7.0	7.5		
8.0	8.5	9.0	9.5	10.0	10.5	11.0	11.5		
12.0									
2.5	5.0	10.0	15.0	20.0					

B

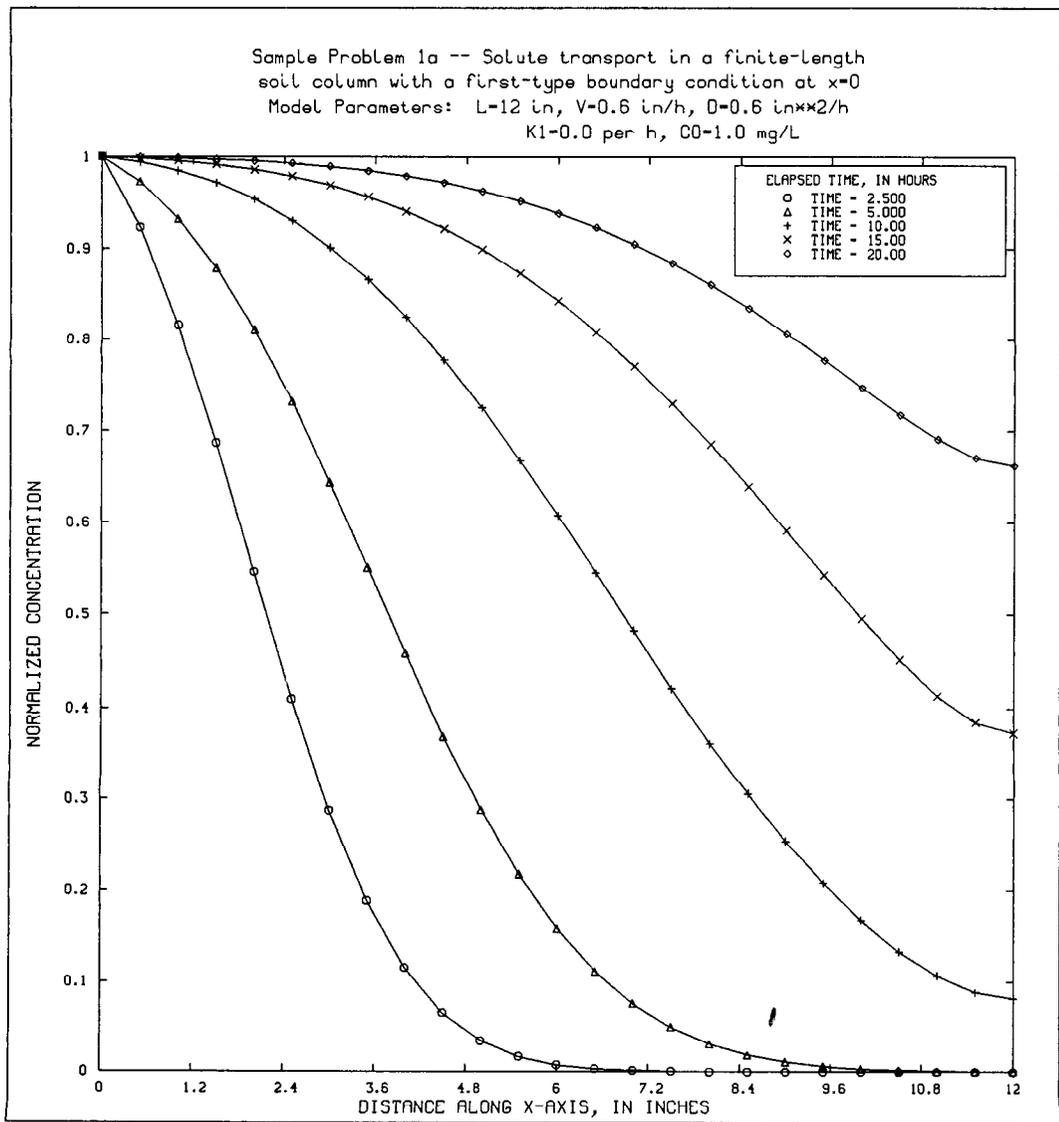


Figure 4.—(A) Sample input data set, and (B) concentration profiles generated by the program FINITE for a conservative solute in a finite-length system with first-type source boundary condition after 2.5, 5, 10, 15, and 20 hours (sample problem 1a).

A

Sample Problem 1b -- Solute transport in a finite-length soil column with a first-type boundary condition at $x=0$
 Model Parameters: $L=12$ in, $V=0.072$ in/h, $D=0.072$ in**2/h
 $K_1=0.0$ per h, $C_0=1.0$ mg/L
 Solute is subject to linear adsorption

MG/L	1	25	04	50	1	IN**2/H	PER HOUR	INCHES	HOURS
1.0	1.0	0.072	0.072	0.072	0.0	0.0	12.0	1.2	
0.0	0.0	0.5	1.0	1.5	2.0	2.5	3.0	3.5	
4.0	4.0	4.5	5.0	5.5	6.0	6.5	7.0	7.5	
8.0	8.0	8.5	9.0	9.5	10.0	10.5	11.0	11.5	
12.0	12.0								
20.0	20.0	50.0	100.0	150.0					

B

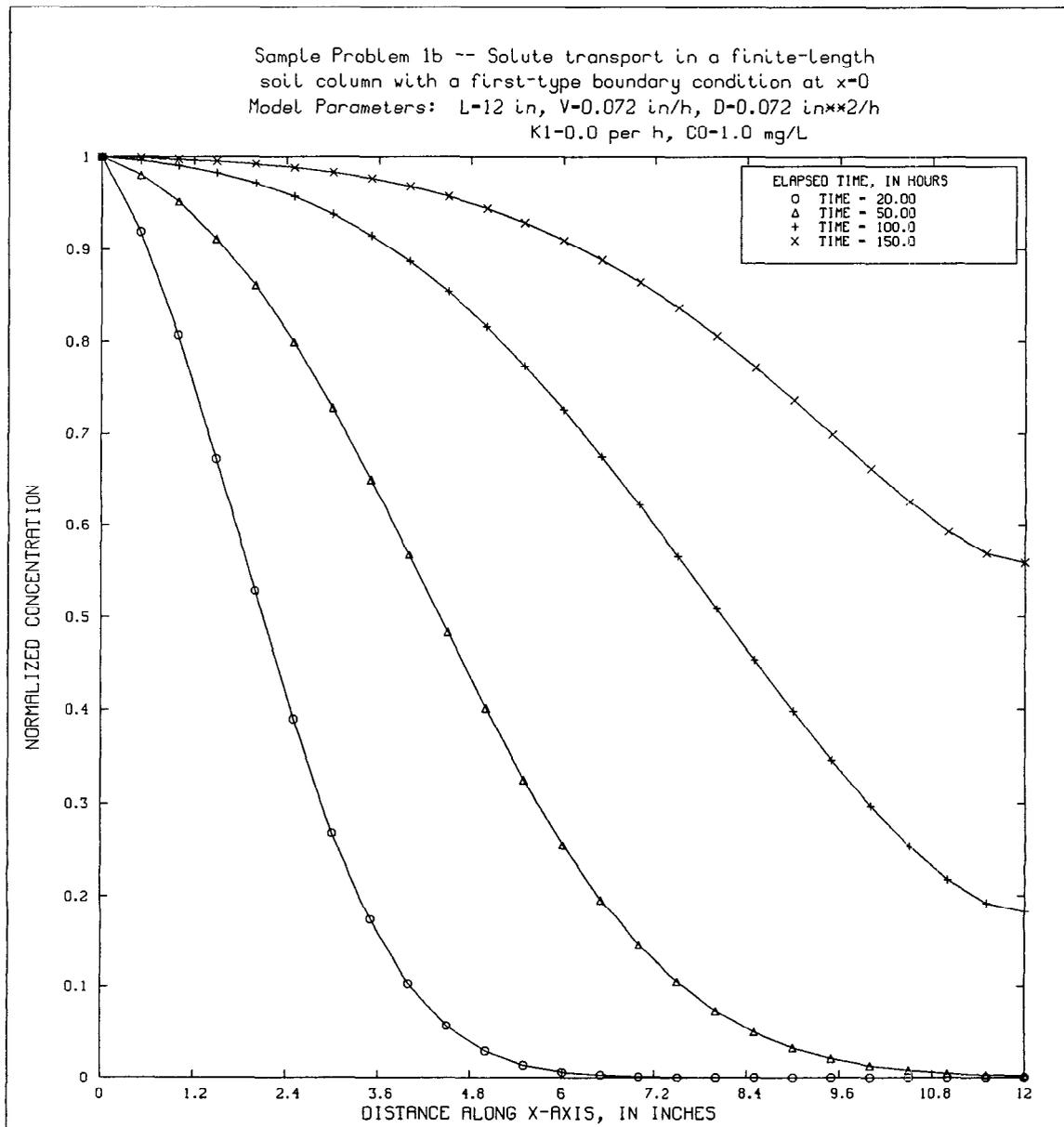


Figure 5. — (A) Sample input data set, and (B) concentration profiles generated by the program FINITE for a solute subject to linear adsorption in a finite-length system with first-type source boundary condition after 20, 50, 100, and 150 hours (sample problem 1b).